SEASONAL CHANGES IN CONCENTRATION AND DISTRIBUTION OF HEAVY METALS IN CREOSOTEBUSH, *LARREA TRIDENTATA* (ZYGOPHYLLACEAE), TISSUES IN THE EL PASO, TX/CIUDAD JUAREZ, MEXICO AREA

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ABSTRACT

We compared seasonal changes in concentrations of four elements, arsenic, cadmium, copper and lead, in samples of various tissues of creosotebush collected in the El Paso, USA/Ciudad Juarez, Mexico region during 1980–81 and 1994–95. Levels in leaf tissue changed seasonally, with concentrations dropping in the spring and late fall, corresponding to the time of leaf drop in the plant. This suggests that most of the heavy metals were simply deposited on the surface of leaves, although data are presented which indicate that internal tissues also have significant levels of heavy metals. These seasonal cycles were less pronounced in the most recent samples. Levels of all four elements in cresotebush were significantly high in the region, as compared to a distant control area. Concentrations of most elements dropped below detection limits within 12 to 30 km from areas of highest concentration. Densities of native Chihuahuan Desert flora and lichens are low in the area, suggesting an apparent negative impact of industrial pollution on the local vegetation. Cadmium and lead levels in creosotebush tissues have dropped over the past 15 years, suggesting that enforcement and strengthening of environmental laws has reduced the air pollution levels in the El Paso area.

RESUMEN

Comparamos los cambios estacionales de las concentraciones de 4 elementos, arsénico, cadmio, cobre y plomo, en muestras de varios tejidos de gobernadora colectados en el área de El Paso y Ciudad Juárez, México durante 1980–81 y 1994–95. Se encontró un cambio estacional de los metales con las concentraciones disminuyendo en la primavera y otoño, que coresponden al momento de la caida de las hojas de la planta. Esto sugiere que hay deposición de los elementos en la superficie de las hojas, aunque presentamos datos de que hay acumulación de metales en los tejidos interiores. Estos ciclos estacionales están menos pronunciados en los últimos años. Los niveles de los elementos son altos en la región, pero están concentrados en un área entre 12 y 30 kilómetros del área con concentraciones más altas. Las densidades de la flora y líquenes en el área son bajas, sugiriendo un impacto negativo de la polución industrial en la vegetación local. Los niveles de cadmio y plomo en los tejidos

SIDA 18(1): 287–296. 1998

ha disminuido en los últimos 15 años, lo que sugiere que la aplicación de las leyes medioambientales ha reducido los niveles de polución en el área de El Paso.

The El Paso/Cd. Juarez area is one of the many regions along the United States/Mexico border which suffers from environmental contamination. The area has been subjected to heavy industrial activity, including smelting and hydrocarbon refining, for over 100 years. This has resulted in an accumulation of heavy metals, especially lead, cadmium, copper and zinc in the local soils (Barnes 1993; Ndame 1993). Arsenic contamination has been previously documented to occur in this region of west Texas (Shields 1991).

These elements and their compounds can cause medical problems in humans and other animals (Elbahri & Benromdane 1991; Louekari et al. 1991). Negative effects of heavy metals on plants have been documented (D'itri 1982; Fernandes & Henriques 1991), including the prevention of the uptake of potassium and phosphorous by roots. Moreover, copper may damage chlorophyll and increase the potency of fungal diseases (Connell & Miller 1984). These effects may eliminate some plant species, with concomitant increases in the abundances of others, thus changing plant community structure. Plants may tolerate heavy metal contamination (Connell & Miller 1984) by excluding metals from sensitive tissues, modifying metabolic pathways to prevent damage or assembling specific enzymes to detoxify heavy metals. The specific effects of heavy metals on the flora of the northern Chihuahuan Desert have not been documented, but Worthington (1989) previously reported a reduction in species richness in native plants in this area, presumably the result of such contamination.

In this investigation, tissues of the dominant Chihuahuan Desert shrub, Larrea tridentata were analyzed, to document continued heavy metal contamination in western Texas. This work is part of a larger study on the effects of heavy metal contamination on the flora and fauna of the northern Chihuahuan Desert and the investigation of bioaccumulation into higher trophic levels.

MATERIALS AND METHODS

We selected a site on the campus of the University of Texas (UTEP) in western El Paso to follow seasonal change in heavy metal concentrations in creosotebush. The site is located within 2 km of a local smelter, which appears to be a point source for the high concentrations of heavy metals in the area. Four elements were included in the analysis: Arsenic, Cadmium, Copper and Lead. Additional sites used to determine the distribution of heavy metals in creosotebush tissues in the region included 62 sampling areas near the border in the United States and six in Mexico within 10 km of the border and of the smelter, of which 52 yielded creosotebush specimens (five repli-

cate bushes at each site). Sites were selected which had native Chihuahuan Desert vegetation located at least 50 meters away from any road. Preliminary analyses showed higher levels of lead next to roadways, which decreased to background levels within a few meters, an effect also noted by Motto et al. (1970), Gratani et al. (1992) and Lebreton and Thevenot (1992).

Leaves were stripped, and twigs were cut from the plants. Roots and trunk tissues were also harvested from plants. Tissues were placed in numbered paper bags and returned to the laboratory. The samples were further cleaned, removing all foreign matter, but were not washed. Bark and exterior tissues were carefully removed from pieces of trunks, to avoid contamination of internal tissues. Tissues from 1980–1981 were collected North of the Education Building on the UTEP campus, as part of another study (Freeman 1982). The tissues were ground and stored dry in glass vials until they were analyzed in 1994. Tissues from 1994–1995 were collected throughout the season from five specific bushes, located in Charlie Davis Park, on the campus of UTEP. This allowed a comparison of the percentages of heavy metals in the tissues of each of the five creosote bushes.

Approximately 20 grams of tissue were placed in a crucible and muffled for three days at 425°C. This relatively low temperature was selected to avoid vaporizing the four elements or their salts (based on the recommendations of Dr. Jim Rayon and Dr. Ken Dodson of the Environmental Protection Agency). After ashing, 100 mg of ash were dissolved in 20 ml of 14% nitric acid (V:V), without filtering. Reagent grade acid and double glass distilled water were used for all solutions. Samples were prepared and stored in glass scintillation vials with polypropylene-lined caps.

Samples were analyzed on a Beckman SpectraSpan 6 direct current plasma atomic emission spectrograph (DCP-AES). We followed the protocol of EPA method 6010 for the inductively coupled plasma emission spectrometer (US EPA 1986). Three of the wavelengths used are those recommended by EPA: 193.696 nm for arsenic, 213.598 nm for copper, and 220.353 nm for lead. The fourth wavelength, 228.802 nm, was substituted for the cadmium analysis to achieve the lowest detection limit. The DCP was calibrated with prepared standard solutions such that the linear calibration curve had an R^2 of at least 0.995. The samples were analyzed by DCP three times and reported the mean and standard deviation of these readings. If the relative standard deviation was greater than 3%, the sample was reanalyzed. Blanks, duplicate samples and prepared standards (spiked samples) were analyzed at least once every ten samples for quality assurance/quality control. Cadmium concentrations in the samples collected in 1994–1995 were close to or below the limits of detection and therefore we have not presented them. After analysis, the DCP solution values were converted to ppm in the original

ash. The detection limits in the ash for this study were 200 parts per million (ppm) for arsenic, 11 ppm for cadmium, 85 ppm for copper and 130 ppm for lead.

Data were plotted with SURFER (Golden Software Inc., Golden Colorado), using the grid method with inverse squared distances and the surface module (Keckler 1995).

RESULTS AND DISCUSSION

Seasonal changes.—Levels of all four elements varied seasonally during both time periods (Fig. 1). Levels were high in the winter and showed a small drop in the spring when there is a combination of minor leaf drop and strong spring winds. The levels increased during the summer, especially during the early sampling period (Figs. 1a, b, c), but later showed a large drop during the fall when creosote lose a large proportion of their leaves (Mackay et al. 1987). Concentrations increased again during the winter months, especially during 1980–1981. Levels of heavy metals were lower in the 1994–1995 samples (Fig. 1d & f). Cadmium and lead were both approximately 4 times higher in 1980–1981, suggesting that enforcement and strengthening of environmental laws has reduced the air pollution levels in the El Paso area.

Seasonal changes in concentrations of all metals during both sampling periods were statistically significant (Table 1). The first harmonics from Fourier analysis of the means (Little & Hills 1972), corresponding to the seasonal effect, were significant for all years, although the patterns were more pronounced during the first sampling period (Fig. 1) and had correspondingly higher F values (Table 1). Other harmonics were statistically significant in 1980–1981, showing the importance of leaf drop in lowering heavy metal concentrations during these years, although there was no pattern in which harmonic was significant after the first. The lack of significance of higher harmonics during the second sampling period suggests that leaf drop was not significant in reducing heavy metal content during those years.

Contamination of tissues.—It appears that large amounts of the heavy metals arsenic, copper and lead are deposited on the leaves, but heavy metals are also incorporated into the tissues of this plant (Fig. 2). Large concentrations of all three elements were found in the roots. The trunks also had high concentrations of the three elements, which were present in the internal tissues as well. The branches and the leaves also had high concentrations of the three elements. These data suggest that heavy metals may be deposited on the outside of the plant, but is also taken up by the roots and incorporated into the woody tissue.

Heavy metal geographical distribution: Levels of the four elements (arsenic, cadmium, copper and lead) in creosotebush ash were elevated adjacent to the United States/Mexico border on the west side of El Paso (Fig.

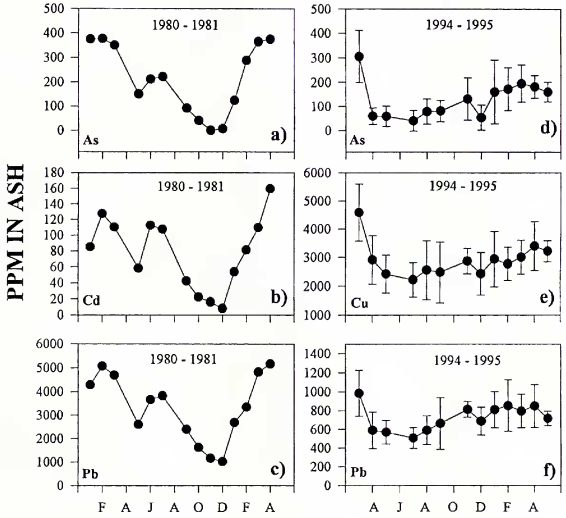

FIG. 1: Seasonal changes in heavy metal concentrations in the leaves of the creosotebush, Larrea tridentata during 1980–1981 and 1994–1995. The gap in 1994–1995 is due to lost samples. Error bars represent standard error of the mean, and are not included in a, b, and c as many of the data points are based on a single sample. The months are abbreviated by a single letter on the x axis.

3). Levels of cadmium were as high as 190 ppm in ash, those of copper reached 5200 ppm and lead levels were as high as 1200 ppm (Fig. 3, note that the surfaces in the figures are close to average values and do not extend to these extreme values). The highest levels of the three elements were recorded on the east side of Mount Cristo Rey (Peak 1 in Fig. 3a), on a small mesa west of McNutt Road (Peak 2 in Fig. 3a), and on the UTEP campus (Peak 3 in Fig. 3a). Levels of all three elements were lower on the southwest side of Mount Cristo Rey, perhaps due to a wind-shadow effect. Levels of all three elements rapidly decreased to the east and fell below detection limits at distances of between 12 and 30 km (Fig. 3).

TABLE 1. Results of Fourier Analysis (Little & Hills 1972) of the periodic functions in Figure 1. Means were used in the analysis.

Source	df	Mean Squares	F Values
		Arsenic, 1980–1981	
First harmonic	2	108121.6	22.2***
error	12	4880.5	
Second harmonic	2	9086.0	2.2 ns
error	10	4039.4	
Third harmonic	2	10400.7	4.2*
error	8	2449.1	
Fourth harmonic	2	5426.9	3.7 ns
error	6	1456.5	
Fifth harmonic	2	1361.7	0.9 ns
error	4	1503.8	
		Cadmium, 1980–1981	
First harmonic	2	8798.9	9.4**
error	12	940.7	
Second harmonic	2	2910.9	5.3*
error	10	546.7	
Third harmonic	2	28.6	0 ns
error	8	676.3	
Fourth harmonic	2	1051.9	1.9 ns
error	6	551.1	
Fifth harmonic	2	1627.3	125.5***
error	4	13.0	
		Lead, 1980–1981	
First harmonic	2	12113720.8	19.9***
error	12	608560.6	
Second harmonic	2	1801911.0	4.9*
error	10	369890.5	
Third harmonic	2	292706.7	0.8 ns
error	8	389186.5	
Fourth harmonic	2	423497.9	1.1 ns
error	6	377749.3	
Fifth harmonic	2	732260.3	3.7 ns
error	4	200493.9	
		Arsenic, 1994–1995	
First harmonic	2	19826.3	5.9*
error	12	3362.4	
Second harmonic	2	1159.2	0.3 ns
error	10	3991.7	
Third harmonic	2	5697.3	1.7 ns
error	8	3309.7	
Fourth harmonic	2	1123.4	0.2 ns
error	6	4733.9	
Fifth harmonic	2	6111.7	3.1 ns
error	4	1978.4	

TABLE 1. continued.

Source	df	Mean Squares	F Values
		Arsenic, 1980–1981	
		Copper, 1994–1995	
First harmonic	2	1168398.7	5.0*
error	12	232963.0	
Second harmonic	2	352562.1	1.8 ns
error	10	198791.8	
Third harmonic	2	231261.4	1.2 ns
error	8	185804.0	
Fourth harmonic	2	118186.9	0.5 ns
error	6	230882.1	
Fifth harmonic	2	267145.6	1.7 ns
error	4	158355.2	
		Lead, 1994–1995	
First harmonic	2	68884.3	7.1*
error	12	9648.9	
Second harmonic	2	8773.5	0.9 ns
error	10	9899.0	
Third harmonic	2	8648.6	0.8 ns
error	8	10399.2	
Fourth harmonic	2	2035.2	0.1 ns
error	6	15975.2	
Fifth harmonic	2	15531.3	0.9 ns
error	4	16863.0	

* = F value of harmonic significant at 0.05 level, ** = F significant at 0.01 level, *** = F significant at 0.001 level, ns = F value not significant.

The areas with the highest values of As, Cu, Cd, and Pb in creosotebush (peaks 1–3, Fig. 3) coincide with the sites of the highest concentrations of heavy metals in the soils (Barnes 1993; Ndame 1993) and in fluff grass (MacKay et al. 1998). In this locale, Pb in the soils exceeds the EPA TCLP (Toxicity Characteristics Leaching Procedures) regulatory limit at a number of sites, and Cd is reported quite close to the limit. The spatial correspondence between elevated metal levels in the soil and the flora is not unexpected. The mechanism of uptake of heavy metals by creosotebush remains to be elucidated.

Densities of native Chihuahuan Desert flora and lichens are low in the area (Worthington 1989, MacKay et al. in prep.), suggesting an apparent negative impact of industrial pollution on the local vegetation. The specific effects of heavy metals on the flora of the northern Chihuahuan Desert are currently being documented. The demonstrated reduction in species richness in native plants in this area is presumably the result of heavy metal contamination from the smelter. These effects may eliminate some species and increase the abundance of others.

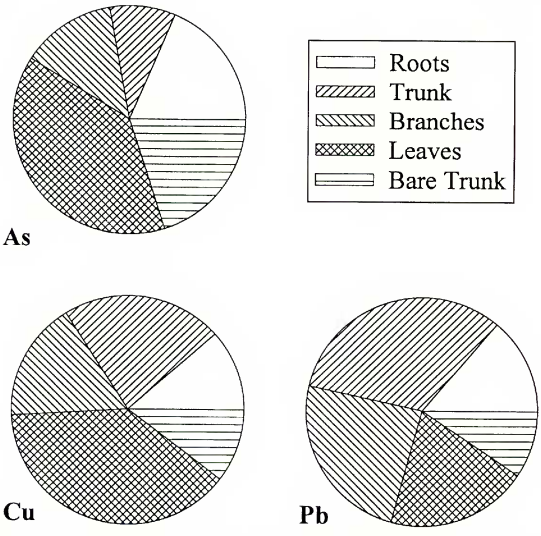

FIG. 2: The distributions of lead, arsenic and copper in specific tissues of the creosotebush from Charlie Davis park on the University of Texas, El Paso campus, El Paso, TX.

ACKNOWLEDGMENTS

We would like to thank the United States Department of Agriculture, especially J.A. Vigil and J. Underwood, for permission to import plant tissues from Mexico. The Texas Department of Parks and Wildlife, especially David Riskind, allowed us to collect plant tissues in the Franklin Mountains State Park. Ken Dodson and Jim Rayon offered suggestions regarding sample preparation. Our research was supported by the Center for InterAmerican and Border Studies of the University of Texas and by the National Science Foundation (HRD 9253021).

REFERENCES

BARNES, B. 1993. An evaluation of metals concentrations in surficial soils, El Paso County, Texas. Unpublished Master's Thesis, University of Texas at El Paso.

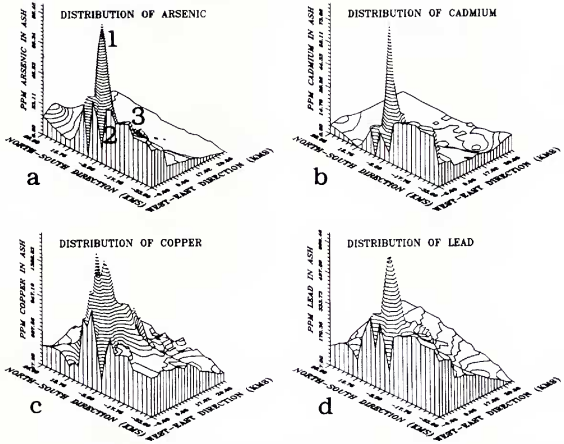

FIG. 3: The distribution of arsenic, cadmium, copper and lead in the El Paso/Ciudad Juárez area. Charley Davis Park on the UTEP campus is located at the origin in the x-y coordinate system (0,0). Peak one corresponds to the east side of Mount Cristo Rey, Peak 2 to a mesa above (west of) McNutt Road and Peak 3 is on the UTEP campus. Detection limits were 200 ppm for arsenic, 11.2 ppm for cadmium, 84 ppm for copper and 132 ppm for lead.

CONNELL, D.W. and G.J. MILLER. 1984. Chemistry and ecotoxicology of pollution. John Wiley and Sons, New York.

D'ITRI, F.M. 1982. Acid precipitation: effects on ecological systems. Ann Arbor Science, Ann Arbor, MI.

ELBAHRI, L. and S. BENROMDANE. 1991. Arsenic poisoning in livestock. Veterinary Human Toxicol. 33:259–264.

FERNANDES, J.C. and F.S. HENRIQUES. 1991. Biochemical, physiological and structural effects of excess copper in plants. Bot. Rev. 57:246–262.

FREEMAN, C.E. 1982. Seasonal variation in leaf nitrogen in creosotebush (*Larrea tridentata* [DC.] Cov.: Zygophyllaceae). SouthW. Naturalist 27:354–356.

GRATANI, L., S. TAGLIONI, and M.F. CRESCENTE. 1992. The accumulation of lead in agricultural soil and vegetation along a highway. Chemosphere 24:941–949.

KECKLER, D. 1995. Surfer for Windows, Ver 6.01, Golden Software, Inc., Golden Colorado.

LEBRETON, L. and D.R. THEVENOT. 1992 Pollution metallique relargable par les aerosols d'origine autoroutiere. Environ. Technol. 13:35–44.

LITTLE, T.M. and F. HILLS. 1972. Statistical methods in agricultural research. Agric. Ext. Service, Univ. California.

LOUEKARI, K., S. VALKONEN, S. POUSI, and L. VIRTANEN. 1991. Estimated dietary intake of lead and cadmium and their concentration in blood. Sci. Total Environ. 105:87–99.

MACKAY, W.P., S. SILVA, S. LORING, and W. WHITFORD. 1987. The role of subterranean termites in the decomposition of above ground creosotebush litter. Sociobiology 13:235–239.

MACKAY, W.P., L. DE LA ROSA, M. ZAVALA, P. SHELTON, J. GARDEA, R. MENA, N. PINGITORE, and G. CRAWFORD. 1998. The distribution of heavy metal contamination in the El Paso, TX/Ciudad Juarez, Mexico area, using fluff grass, *Erioneuron pulchellum*, as an indicator organism. Proc. Chih. Desert Res. Inst. (In Press).

MOTTO H.L., R.H. DAINES, D.M. CHILKO, and C.K. MOTTO. 1970. Lead in soils and plants: its relationship to traffic volume and proximity to highways. Environ. Sci. Technol. 4:231–237.

NDAME, E.C. 1993. Heavy metals in soils in the vicinity of the University of Texas at El Paso campus (El Paso, Texas). Unpubl. Master's Thesis, University of Texas, El Paso.

SHIELDS, J. 1991. Ambient air arsenic levels along the Texas - Mexico border. J. Air Waste Manag. Assoc. 41:827–831.

US ENVIRONMENTAL PROTECTION AGENCY. 1986. Test methods for evaluating solid waste (third edition). Washington, D.C.

WORTHINGTON, R.D. 1989. Effects of El Paso pollutants on the lichen, moss, and winter annual flora on andesite rock formations. In: P. Ganster and H. Walter, eds. Environmental hazards and bioresource management in the United States/Mexico borderlands, UCLA Latin American Center Publications. Los Angeles. Pp. 105–115.